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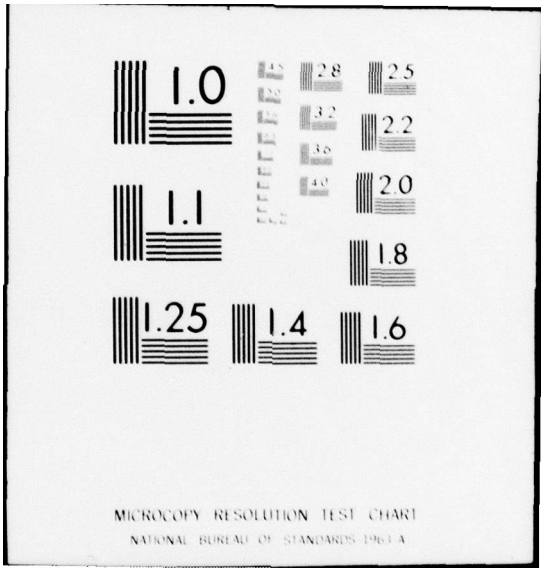
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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER (11) 12925.2-C (12) ARO	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) (6) Surface States Associated with Chemisorbed Species	5. TYPE OF REPORT & PERIOD COVERED: Final Report: 1 Apr 75 - 31 Mar 78
6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s) (10) S. Roy Morrison	8. CONTRACT OR GRANT NUMBER(s) (15) DAAG29-75-C-0017 DAHC04-75-C-0017
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Stanford Research Institute, International, Menlo Park, California 94025	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS: U. S. Army Research Office, P. O. Box 12211, Research Triangle Park, NC 27709	12. REPORT DATE (11) May 78 (13) NUMBER OF PAGES 3
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) (12) 6 p.	15. SECURITY CLASS. (of this report) unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

(9) Final rept. 15 Mar 75-15 Mar 78,

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

DDC RECEIVED JUN 20 1978 F

18. SUPPLEMENTARY NOTES

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Two areas of interest were investigated, first, surface states on semiconducting powders, and second, states associated with defects in passivating oxide films, emphasizing SiO_2 on Si.

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Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

May 1978

Final Report
For the period from 15 March 1975 to 15 March 1978

SURFACE STATES ASSOCIATED WITH CHEMISORBED SPECIES

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PROGRESS REPORT

1. ARO PROPOSAL NUMBER: DAH C04-75-C-0017

2. PERIOD COVERED BY REPORT: 15 March 1975 to 15 March 1978

3. TITLE OF PROPOSAL: SURFACE STATES ASSOCIATED WITH CHEMISORBED SPECIES

4. CONTRACT OR GRANT NUMBER: DAH C04-75-C-0017

5. NAME OF INSTITUTION: SRI International

6. AUTHOR(s) OF REPORT: S. Roy Morrison

7. LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED UNDER ARO SPONSORSHIP DURING THIS PERIOD, INCLUDING JOURNAL REFERENCES:

(see Appendix)

8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED DURING THIS REPORTING PERIOD:

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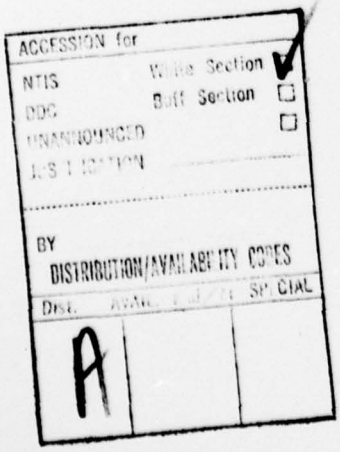

REVIEW OF PROGRAM, SURFACE STATES
ASSOCIATED WITH CHEMISORBED SPECIES

During the three year period covered by this final report, two areas of interest were investigated, first, surface states on semiconducting powders, and second, states associated with defects in passivating oxide films, emphasizing SiO_2 on Si.

In the studies of surface states on semiconducting powders, the program was viewed to some extent as the basic research phase of a development of gas sensors. Thus, the particular systems studies were chosen with the concept in mind of investigating gas/surface state interaction. For example, the interaction of gaseous bases with acid sites on solids[1*] was studied. In this study we were able to show that in many cases sites on an oxide surface play a dual role, acting both as acid sites and as surface states. Because of this dual role, the adsorption of gaseous bases on these sites causes electrical changes in the semiconductor. In a separate study[2] of the important catalyst chromia, Cr_2O_3, we were able to show that unoccupied adsorption sites behave as surface states. Specifically coordinatively unsaturated Cr^{+3} ions at the surface that act in π bonding CO or that act as sites for oxygen adsorption as O_2^- or O^- are, when no adsorbed gas is bonded to them, donor surface states. The physical picture of a surface state donor and the chemical picture of a donor-acceptor complex:

$$Cr^{+4} - O_2^-$$

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*For references, see Publications.

are thus directly reconcilable. Of interest also is the observation that the surface donor level of the Cr^{+3} was found to be 0.3 eV higher than the bulk Cr^{+3} levels (the valence band) and the surface ion is thus highly reactive with adsorbing gaseous oxidizing agents.

Our studies of silica on silicon had two objectives, one to examine flaws in the silica, the other to study surface states on the silica. To date only the first has been pursued. In particular, we have examined oxygen ion vacancies (Si^{+3} sites) introduced by high-temperature treatment of the grown SiO_2 film in vacuum. The SiO_2 prepared in this way behaves as if the defects form a conducting impurity band, and the SiO_2-covered silicon becomes an active and reproducible electrode exchanging electrons with many ions in solution.

This study has not yet been submitted for publication--the impurity band interpretation and the interpretation of the electrode processes that follows is a substantial divergence from normal electrochemical models, so must be strongly supported by experimental evidence. In our next series of experiments we will vary the defect concentration at constant oxide thickness (vary the temperature of the vacuum treatment) to define the model more accurately. Independent of the final model, however, this unusual "glass electrode" with its electronic conductance mechanism, will be of great interest.

Appendix

Publications During the Period Covered by this Report

1. Surface States Associated with Acid Sites on Solids, Surface Sci. 50, 329 (1975).

2. Surface States on a Chromia Catalyst, J. Catalysis 47, 69 (1977).

3. The Study of Semiconductor Using Electrochemical Techniques, to be published in Proc. 5th Conf. on the Physics of Compound Semiconductor Surfaces, Los Angeles, 1978.

4. Dislocations in ZnO as Channels for Electron Transfer from Surface Species, Nat. Bu. Standards Special Public. 455, "Electrocatalysis on Non-Metallic Surfaces," ed. A. D. Franklin, November 1976.

5. U.S. Patent No. 4,039,941, Gas Sensor, issued August 2, 1977.

Review Articles and Books During this Period. These were not directly sponsored by ARO, but drew heavily on the background of our ARO research:

1. Semiconductor Surfaces, p. 203 of "Treatise on Solid State Chemistry" Vol. 6B, ed. N. B. Hannay (Plenum, New York, 1976).

2. Theory of Adsorption, p. 221 of "Surface Physics of Phosphors and Semiconductors," ed. E. G. Scott and C. E. Reed (Academic, London, 1975).

3. "Catalysis-on Top of Semiconductors" Chemtech 7, 570 (1977).

4. "The Chemical Physics of Surfaces" (Plenum, New York 1977).